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TORSION IMPREGNATED CLOTH ANALYSIS (TICA)

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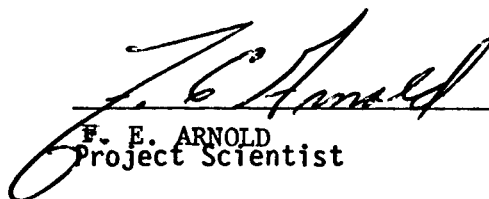WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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Torsion Impregnated Cloth Analysis (TICA) uses fiber glass cloth as support for polymeric resins and measures the cloth-resin composite's in-phase and out-of-phase dynamic mechanical responses with a Rheometrics Mechanical Spectrometer. The TICA thermoscan results of a thermo-plastic were compared with that of the neat material. A similar comparison was made between the isothermal curing results of a thermosetting resin and the corresponding parallel plate and TBA measurements. The peaks associated with the vitrification were verified to correspond to those in the glass transition region.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins". It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Labortory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the ML Project Scientist. Co-authors are Dr. C. Y-C. Lee, Dr. I. J. Goldfarb, Air Force Wright Aeronautical Laboratory, Polymer Branch (AFWAL/MLBP) and Mr. J. D. Henes; University of Dayton Research Institute.

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INTRODUCTION

In polymeric development programs, there are always needs to characterize the mechanical properties of the materials. Depending on the state of the material, a different experimental mode is required. For thermoplastic materials, the state is mainly a function of temperature, so at low temperature region, the solid state experimental mode is appropriate, and at high temperature, the liquid mode is used. But for thermosetting systems, the state of the material is also a function of the cure, which may vary during an experiment. So a material may start out at the beginning of the experiment as a solid, transition into the liquid state and solidify again. To change experimental modes during the course of the experiment is impractical. Techniques that can measure both the solid and liquid states are desired in such situations.

Torsional Braid Analysis (TBA) (Reference 1) has been used successfully in characterizing polymers' mechanical properties in both bulk and liquid state, as well as studying the cure behavior of thermosetting systems (Reference 2). The specimen, which is a glass braid bundle impregnated with the resin of interest, is set in free oscillatory motion. The frequency and decay characteristics of this motion yield rigidity and loss tangent information about the composite. This work reports experiments similar in nature to TBA, but the detection mode is forced torsion rather than free oscillation. The specimen is mounted on a Rheometrics Mechanical Spectrometer (RMS) which is run in the torsional bar mode. Because of the difference in the detection mode and thus the forms of the results, another name, Torsion Impregnated Cloth Analysis (TICA), is proposed for the latter technique, so the results from the two experiments can be distinguished.

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The TICA technique will be demonstrated with a thermoplastic and a thermo-setting resin and the results will be compared with the neat form properties as well as comparable TBA data.

EXPERIMENTAL

The resin to be studied was dissolved with appropriate solvents and a fiber glass cloth about 10 cm wide was wetted with the solution. After it had been hung in an exhaust hood overnight, the cloth was evacuated for solvent extraction at room temperature for a week before use. The cloth was cut into rectangular patches of 10 X 7.5 cm, and they were folded into strips of 10 cm long and 1.25 cm wide, with the cut edges folded inside the strips. Three strips were stacked together to compose one TICA specimen. (See Appendix I.)

Fixtures were fabricated to hold the TICA specimen in the sample chamber of the RMS. The fixtures are stainless steel plates of dimension: 17.8 mm x 12.6 mm x 2.3 mm (length x width x thickness). The cloth ends were sandwiched by two fixtures plates held together by a screw at the center. Aluminum foil was used to separate the fixture from the cloth so that the cured resin will bond to the foil instead of the fixtures. The resulting specimens had dimensions at both ends similar to that of Torsion Bar specimens of the RMS, and they are mounted on the sample holding chucks of the RMS the same way as the torsion bars. The specimen is held at both ends between the servo motor and transducer of the RMS in an environmental chamber. A sinusoidal strain is induced by the oscillatory motion of the servo motor. The resultant sinusoidal stress is detected with the stress gauge, whose output voltage is tapped into a frequency analyzer. By comparing stress and strain waveforms, the in-phase (a) and out-of-phase (b) responses of the specimen are calculated. The environmental chamber is capable of a temperature range from -150°C to 400°C.

RESULTS AND DISCUSSION

TICA Study Of Thermoplastics

The temperature scan of a polyphenylsulfone (Radel, Union Carbide Corporation) TICA sample at three frequencies (1, 10, 100 rad/sec) is shown in Figure 1. The in-phase and out-of-phase responses (a and b respectively), together with their ratio, tan δ (b/a), are shown for each frequency. At the region below Tg, the low frequency measurement at one rad/sec exhibits more noise than those from the 10 and 100 rad/sec. For the b components of the two higher frequencies, three peaks can be identified below Tg vs only one peak in the one rad/sec measurement. The peaks occurred at about -100°C, 50°C, and 150°C.

The Radel mechanical behavior has been characterized in neat form (Reference 3). Radel powder was hot-pressed at 300°C into a rectangular bar, and its dynamic response was measured with the RMS in the rectangular bar mode. Two transitions below Tg were observed and they correspond to the TICA peaks observed at -100°C and 50°C and they were labeled as γ and β transitions, respectively. The temperature of the peak maxima from both the TICA experiment and the rectangular bar experiments are listed in Table I.

It is interesting to note the TICA peaks at 150°C all have their maxima occurring at the same temperature. If the peaks are due to some molecular motion transition, by energy barrier consideration, one would expect the lower frequency measurement to yield a peak maximum at a lower temperature. The peaks at -100°C and 50°C do exhibit such characteristic behavior. It is possible that the peaks at 150°C result from the presence of residual solvent in the TICA sample. The maxima can be explained by some kinetic phenomena,
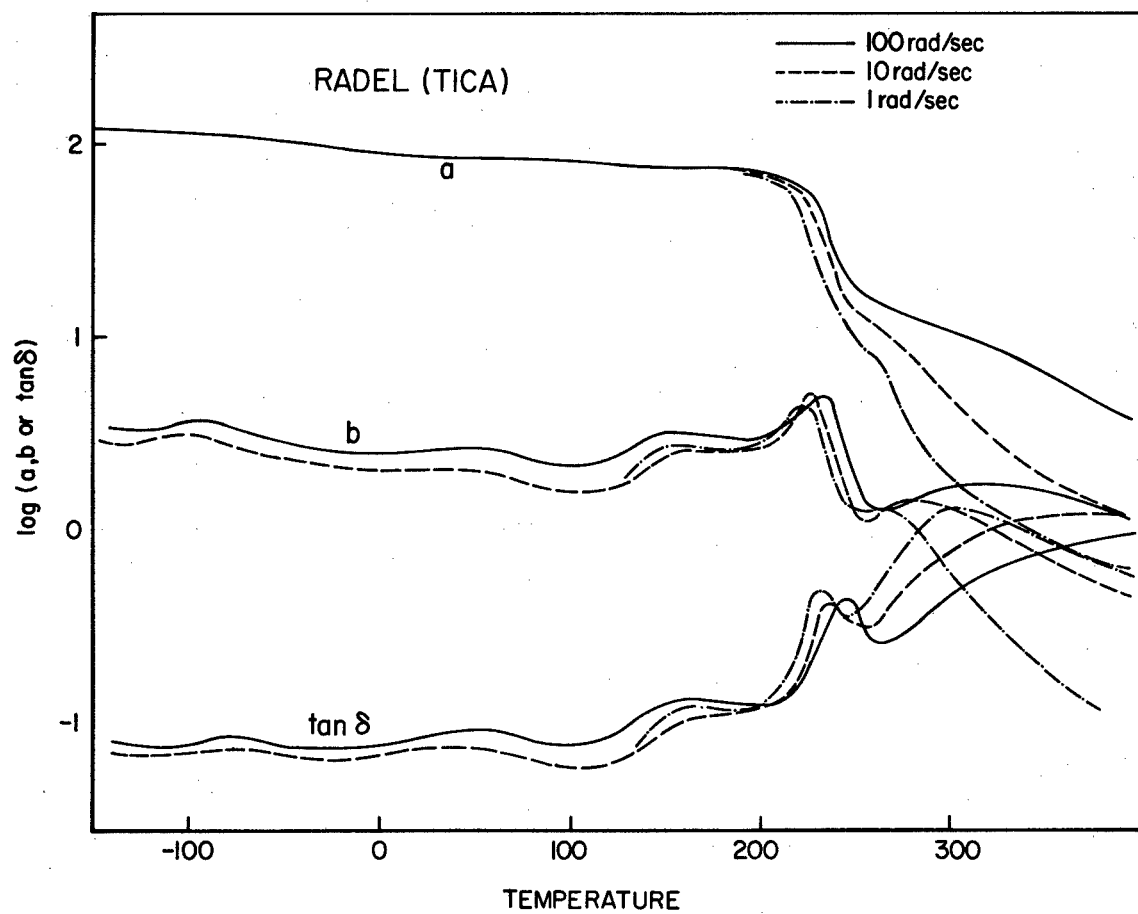
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Figure 1: The Thermoscan of a TICA Specimen of Polyphenylsulfone.

like residual solvents diffusing out of the sample whose effect on the sample behavior at all frequencies appear at the same temperature. On rerun of the same sample, those peaks at 150°C did not appear. Detailed discussion of this kinetics effect is outlined in Reference 4.

On reruns of both the TICA and the neat bar samples, the transitions at the 50°C region also disappear. It is uncertain whether this transition is also solvent related. It is unlikely, however, because the bar sample had undergone heat treatment above Tg during the hot-press molding. J. Heijboer (Reference 5) had reported similar transitions in polysulfone at about 60°C whose peak intensity can be suppressed with heat treatment. The transition at 50°C has been characterized to have an activation energy of 17 kcal/mole; and that of the transition at -100°C is 10 kcal/mole (Reference 3).

The TICA behavior at the glass transition temperature agrees qualitatively with that observed with the neat bar sample: a substantial decrease in the in-phase component accompanied by a peak in the out-of-phase component. The neat bar G' decreases by three orders of magnitude, but the TICA decreases by only one. Neat bar loss tan δ peak has a maximum of about 1.5 while the TICA maximum is only 0.65. In spite of these differences, the b maxima and the tan δ maximum temperatures at all frequencies agree well with that from the neat bar experiment. The values are listed in Table I.

Measurements of the neat bar behavior about 265°C are not available because of the sample rigidity problem. Instead, Radel has been characterized in the parallel plates mode on RMS (Reference 3) from 245°C to 380°C. The data are represented in Figure 2. Except for the requirement of a slight vertical shift on the log plots, the neat bar data and the parallel plates data can be superimposed in the overlapping temperature region, from 245°C to 265°C. The result of such a superposition is shown in Figure 2-D.

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TABLE I

TRANSITION TEMPERATURES[a] OF POLYPHENYLSULFONE

Transition	Frequency (rad/sec)	Neat Resin[b]	TICA
T > Tg	1	247	265
	10	260	280
	100	278	325
Tg	1	223(228)	222(228)
	10	226(231)	225(232)
	100	230(237)	230(237)
β	1	15	---
	10	32	44
	100	70	58
γ	1	-120	---
	10	-105	-112
	100	- 95	- 98

a All temperature values are in $^{\circ}C$; all values refer to the loss modulus maxima except those in brackets which denote the values at the tan δ maxima.
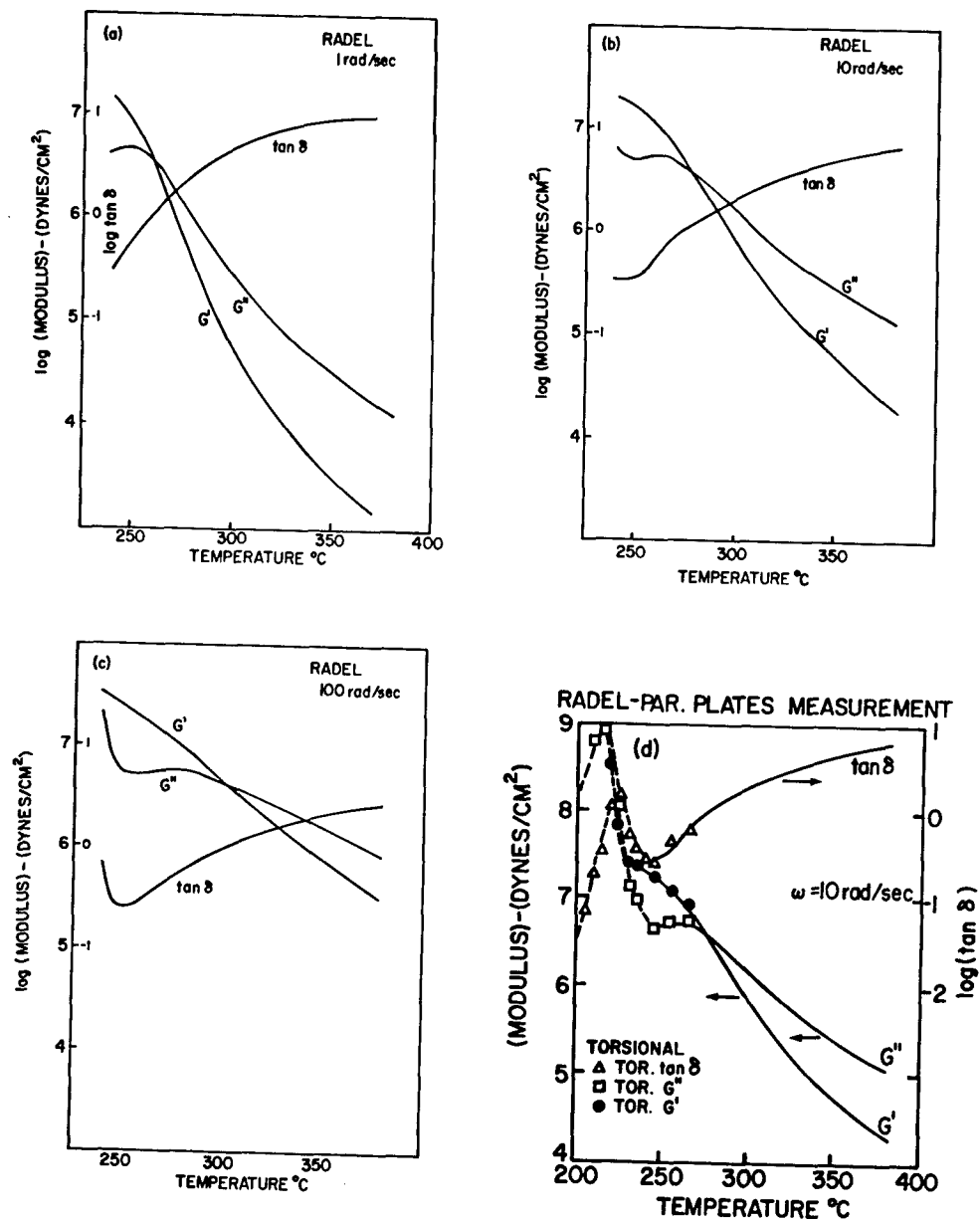
b Reference 3.

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Figure 2: The Parallel-Plates Data of Polyphenylsulfone. The data
for 1 rad/sec, 10 rad/sec, and 100 rad/sec are displayed
in figures (a-c) respectively. The overlapping region
between the parallel plates data and torsional bar data
for 10 rad/sec is displayed in (d).

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The TICA data above Tg show maxima in the b component at all three frequencies. G" maxima are also observed in the parallel plates measurements. The presence of such G" maxima are not surprising considering the possibility of molecular entanglement (Reference 5). The TICA peak maximum temperatures are consistently higher than the corresponding parallel plates values (see Table I). This discrepency may be the result of the supporting matrix-resin interaction. In this region, the contribution of the interaction effect to the overall response of the sample will be proportionally larger than in the glass transition region because the resin is in a lower viscosity state.

In the parallel plates measurement, in spite of the presence of the G" maxima, there are no corresponding tan δ maxima in this region. However, in the TICA results, the one rad/sec measurement shows a tan δ maximum at about $300^{\circ}C$, and the 10 rad/sec at about $365^{\circ}C$. It seems reasonable that those tangent peaks are due to the effect of matrix resin interaction as suggested by Nielsen (Reference 7), and Neumann, et al, (Reference 8). The matrix-resin interaction affects the in-phase and out-of-phase responses differently, thus causing a superficial maximum in their ratio. It is not clear, however, if the TBA's $T_{\ell\ell}$ transition observed in atactic polystyrene (8) corresponds to the same phenomenon. In TBA, the T > Tg peak is smaller than the Tg loss peak, but in this experiment, the order is reversed.

TICA Study of a Thermosetting Resin

The application of TBA to characterize thermosetting resins during cure has been reported (Reference 10). For an isothermal curing experiment at a temperature where the uncured resin is in the liquid state, the system will go from the liquid state to the rubbery state, then to the glassy state. In such a TBA isothermal curing experiment, two peaks have been observed with the plot of log decrement as a function of time. The first peak has been associated with

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gelation; and the second peak has been identified with vitrification.

The epoxy resin used in these experiments contains a multifunctional epoxy (tetraglycidylmethlene dianiline), an aromatic diamine curing agent (diaminodiphenylsulfone) and organometallic catalyst (boron triflouride complex) (10). erence 11). Figure 3 is a plot of the TICA results, a, b and tan δ, as a function of log time, curing at 155°C. The tan δ also shows two peaks (at 1400 and 2500 sec.), just like TBA. In addition, the b component also shows a maximum at 4850 sec. Normally, an increasing temperature scan of a polymer system through the glass transition region will show the G" maximum occuring at a lower temperature than the tan δ maximum. The isothermal curing around the vitrification region is like a decreasing temperature scan. So the tan δ maximum should occur before the b maximum. A multi-frequency run of an isothermal TICA experiment also reveals the high frequency maxima always preceed the corresponding lower frequency maxima. The shape of the curves do not resemble, except in the qualitative sense, the mirror image of a conventional dynamic mechanical spectrum at glass transition region, because the x-axis of the plot is no longer governed by temperature variation, but by the kinetics of curing of the highly viscous system around Tg.

Like the T > Tg tan δ maximum, the gel peak is not associated with any discernable b maximum. The dynamic response of the neat resin during isothermal cure at 155°C has been measured in the parallel plates mode and is shown in Figure 4. At the region where the TICA gel peak appears, neither G" (α η') nor tan δ shows a peak, but a distinct, reproducible change in slope of the tan δ is noted at 1400 sec. The relationship between the slope change and the appearance of the TICA tan δ peak is unclear, however, the evidence suggests that the first tan δ peak (at least in the TICA experiment) is probably due to the presence of the supporting substrate.
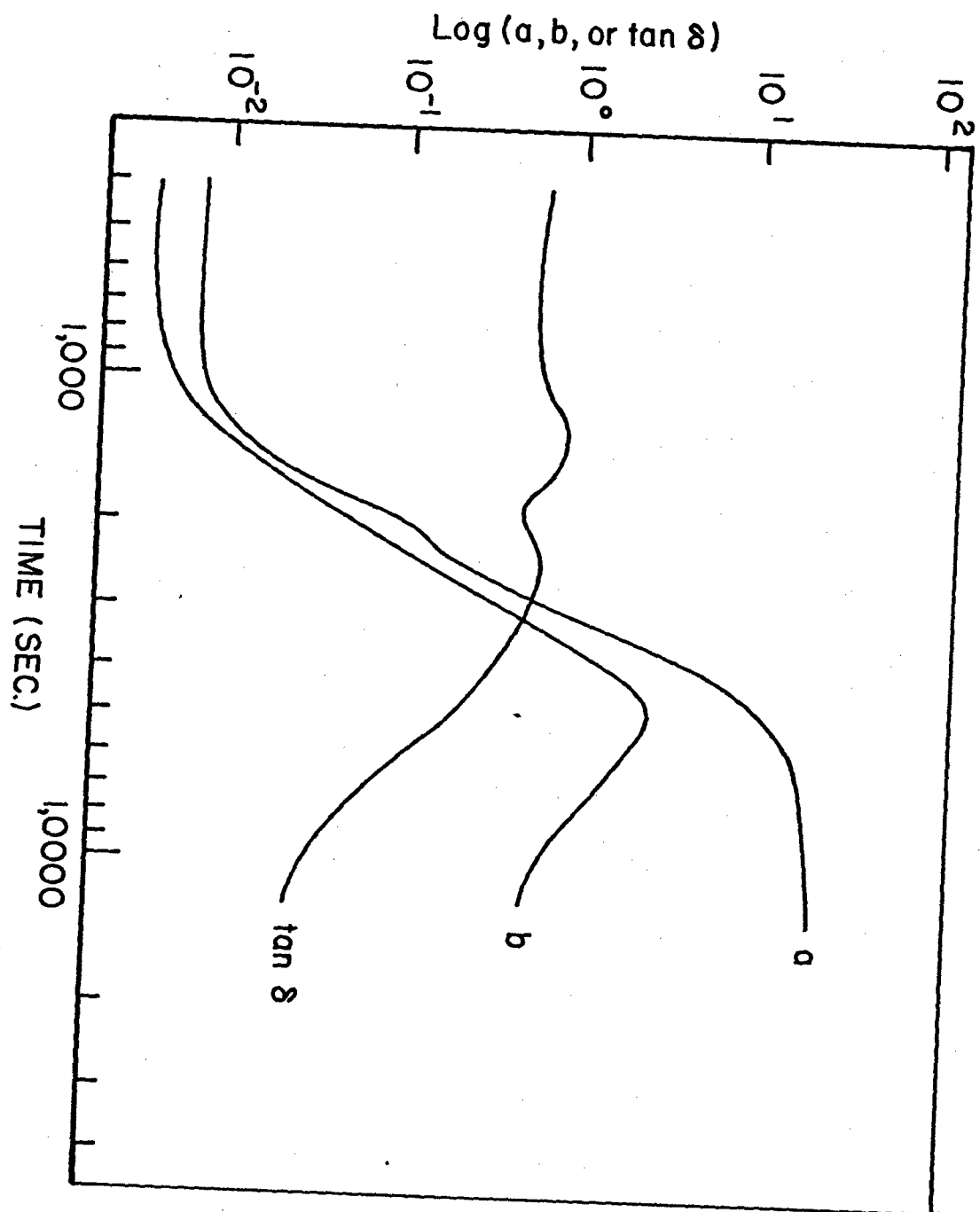
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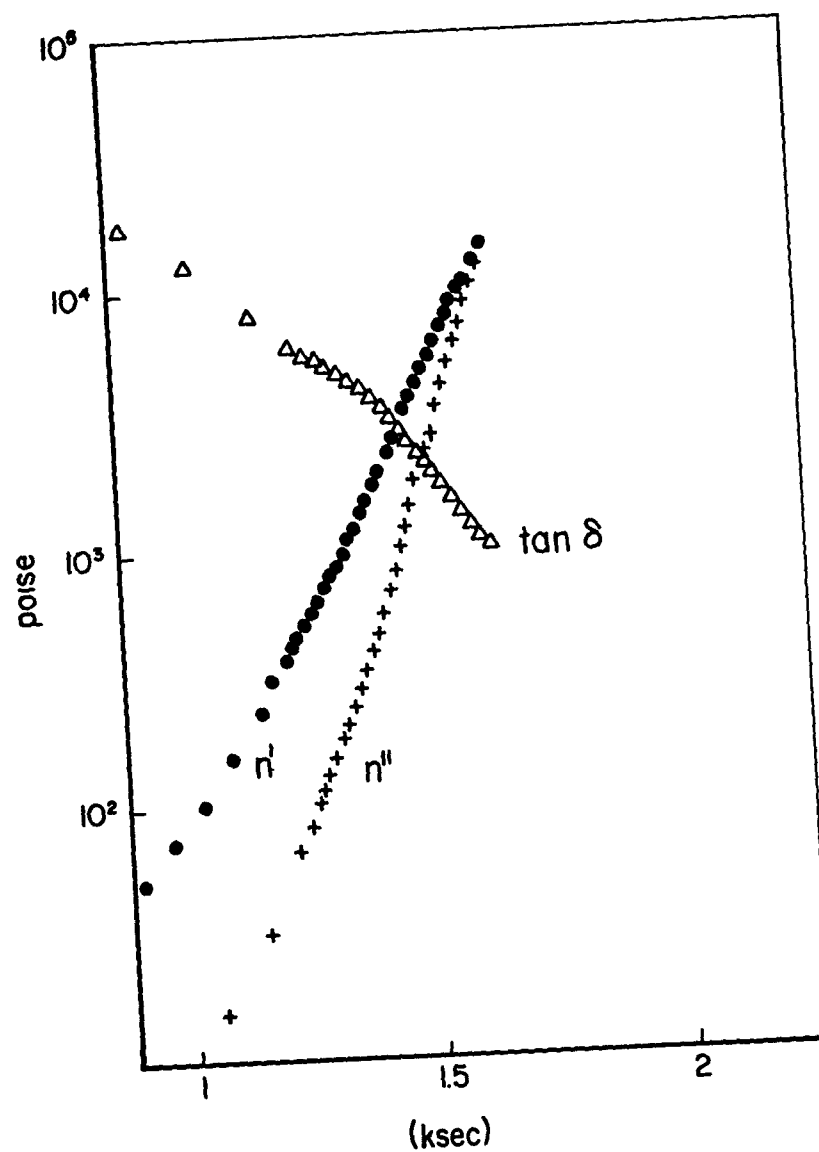Figure 3: The Results of a TICA Isothermal Cure at 155°C.

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igure 4:   The Parallel Plates Data of Isothermal Epoxy Cure at
           155°C.

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A TICA specimen which has been stored at room temperature for five months did not show the gel peak when cured at 94°C. Another specimen from the same batch, however, showed a gel peak at 150°C curing. This suggests that the "gel" peak observed here is not the same as the gelation of the conventional theory, which is a critical conversion condition independent of temperature. As the resin is cured, not only is the Tg being advanced as a result, the "gel" peak, which may actually be an isoviscous state phenomenon as suggested by Lewis, et al (Reference 7), is also pushed to a higher value. For this batch of specimens, the long period of storage time at room temperature must have advanced this maximum to between 94°C and 150°C.

Another specimen was cured at 94°C for 2½ hours. At that time, both a and b components of the three frequencies were rising slowly. The 1 and 10 rad/sec tan δ were rising also, but the 100 rad/sec tan δ had leveled off to a maximum. A temperature scan of this specimen between 0°C to 95°C showed a 100 rad/sec tan δ maximum at about 88°C (see Figure 5). Subsequently, the specimen was cured again at 94°C for over fourteen hours. The 100 rad/sec b component had reached a maximum and was decreasing. The 10 rad/sec b component was leveling off with the 1 rad/sec b component still increasing. A subsequent scan of this specimen (Figure 6) showed the b maxima at 85°C (1 rad/sec), 93°C (10 rad/sec) and 102°C (100 rad/sec). This clearly demonstrates that both the tan δ peak and b maximum observed in TICA are associated with vitrification. The long time span separating the tan δ maximum and the b maximum is indeed due to the difficulties of curing in the viscous state. Using the b maximum temperature as the criterion to define Tg, the experiment also shows that one can prepare specimens with predetermined Tg's by curing the specimen at the desired Tg temperature and stopping the cure when the b maximum is reached.
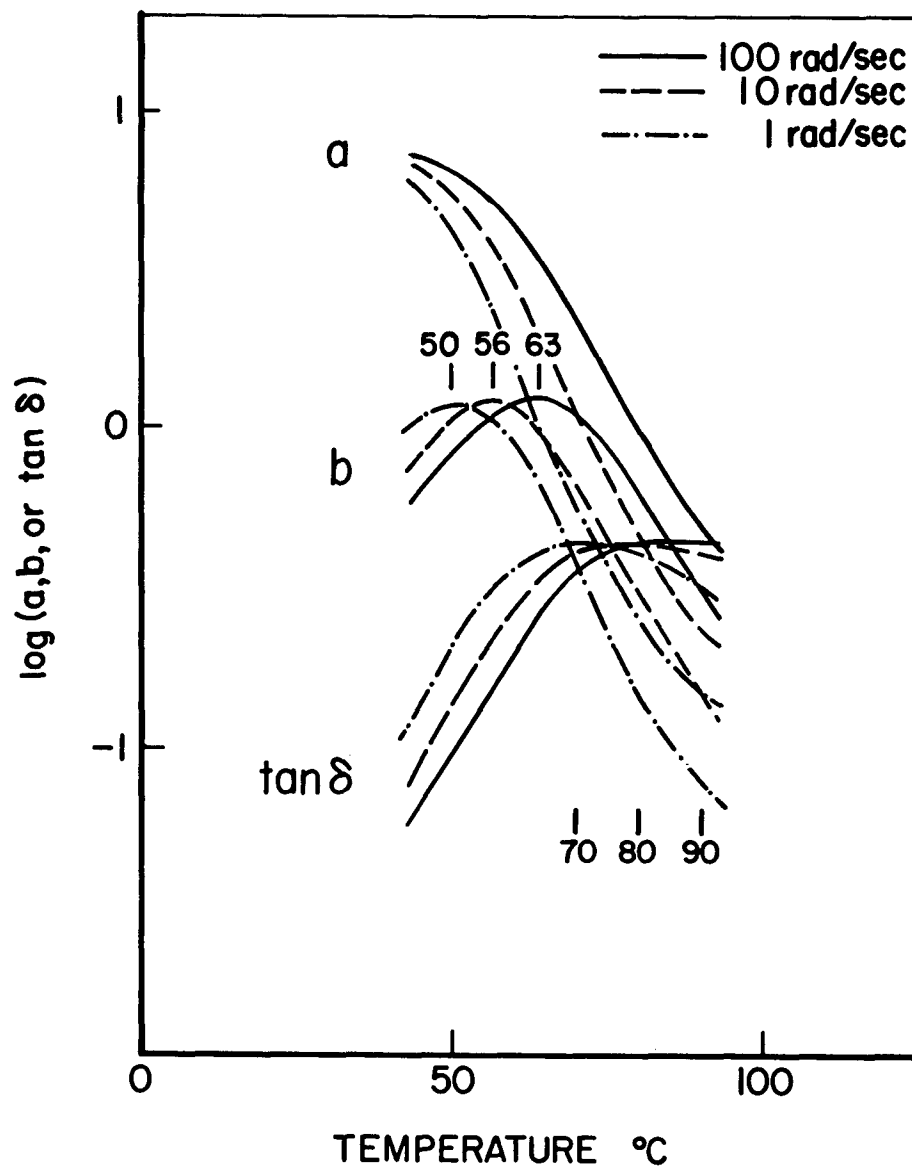
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Figure 5: The Thermoscan Results of an Epoxy TICA Specimen After Curing to Tan δ Maximum (100 rad/sec) at 94°C.

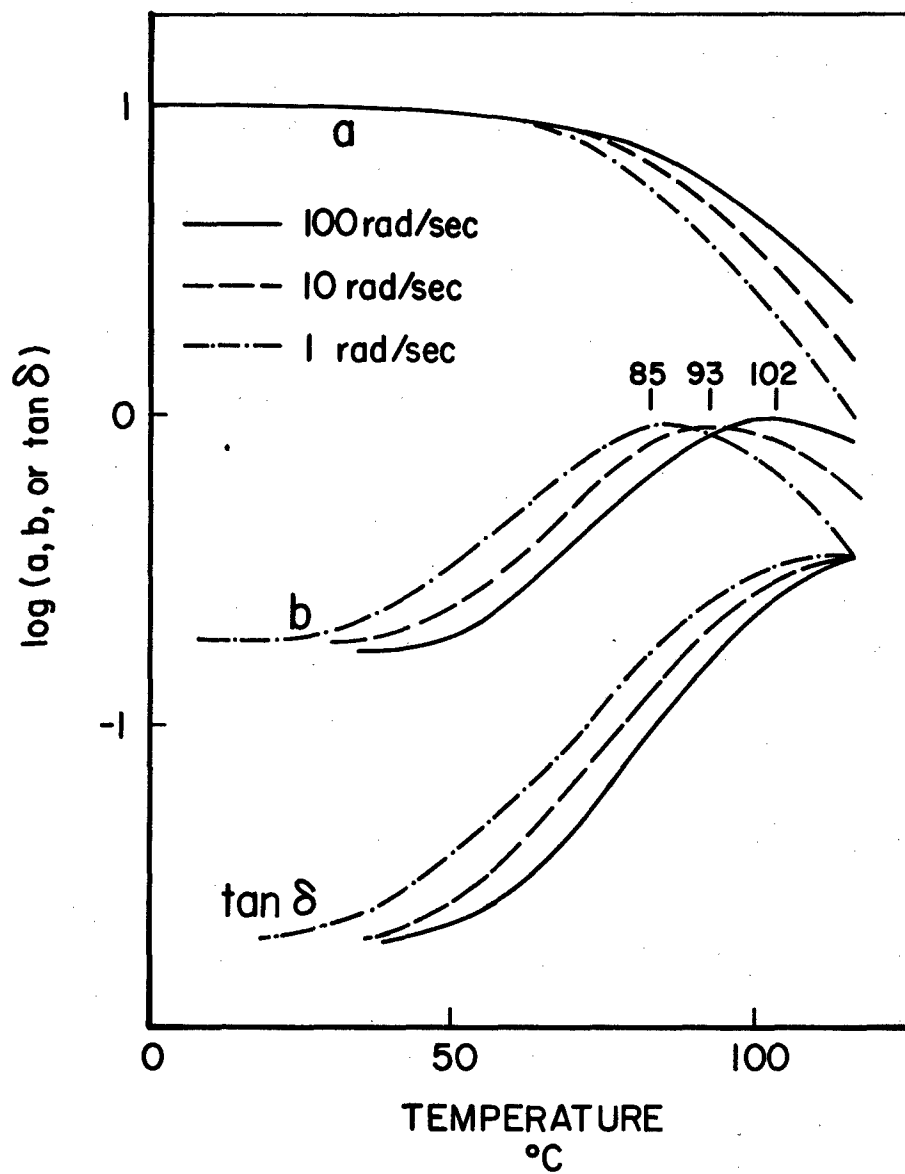Figure 6: Thermoscan Results of an Epoxy TICA Specimen After Curing to b Maximum (10 rad/sec) at 94°C.

So for every set of TICA isothermal cure curves, three points in time can be identified. The time at the first tan δ maximum is labeled as t_{gel} as in the TBA experiment. The second tan δ maximum is labeled at t_δ and the b maximum denoted as t_{vit}. Isothermal cures have been carried out at 135°C, 155°C, 175°C, and 207°C. The results from these curves are listed in Table II, and are plotted in Figure 7 as a cure phase diageam (Reference 10). All values reported are for 10 rad/sec (1.6Hz) measuring frequency.

For the TICA isothermal curing experiments, the specimens were mounted on the RMS at room temperature, and the temperature was quickly increased to the experimental value. The time at the beginning of the temperature increase was considered as time zero. Four to five minutes was needed for the temperature to equilibrate to the desired temperature. The results reported here are not very reproducible, because different experiments have different amount of temperature overshoot during the heat up, which could affect the three identification times noticably. Currently, a heat-up procedure with a temperature increasing rate of 10°C/5 second is being used in this laboratory which can minimize the amount of overshoot, and results in a reproducible profile of temperature increase. With this new procedure, the three times are much more reproducible. Because of this heat-up requirement, the values for short times are not reliable.

The cure phase diagram of TBA has only two points of identification (neglecting the tan δ minimum). Results of the TBA experiments on the same material (Reference 12) are also plotted in Figure 7. Since the TBA's log decrement is supposedly propoetional to tan δ, comparison should be made with the tan δ values of TICA. The agreement between the two sets of data are poor. The discrepencies at high temperatures can be attributable to the heat-up procedure used in the TICA experiment, because at those temperatures the heat-up times

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TABLE II

RESULTS FROM ISOTHERMAL CURE CURVES

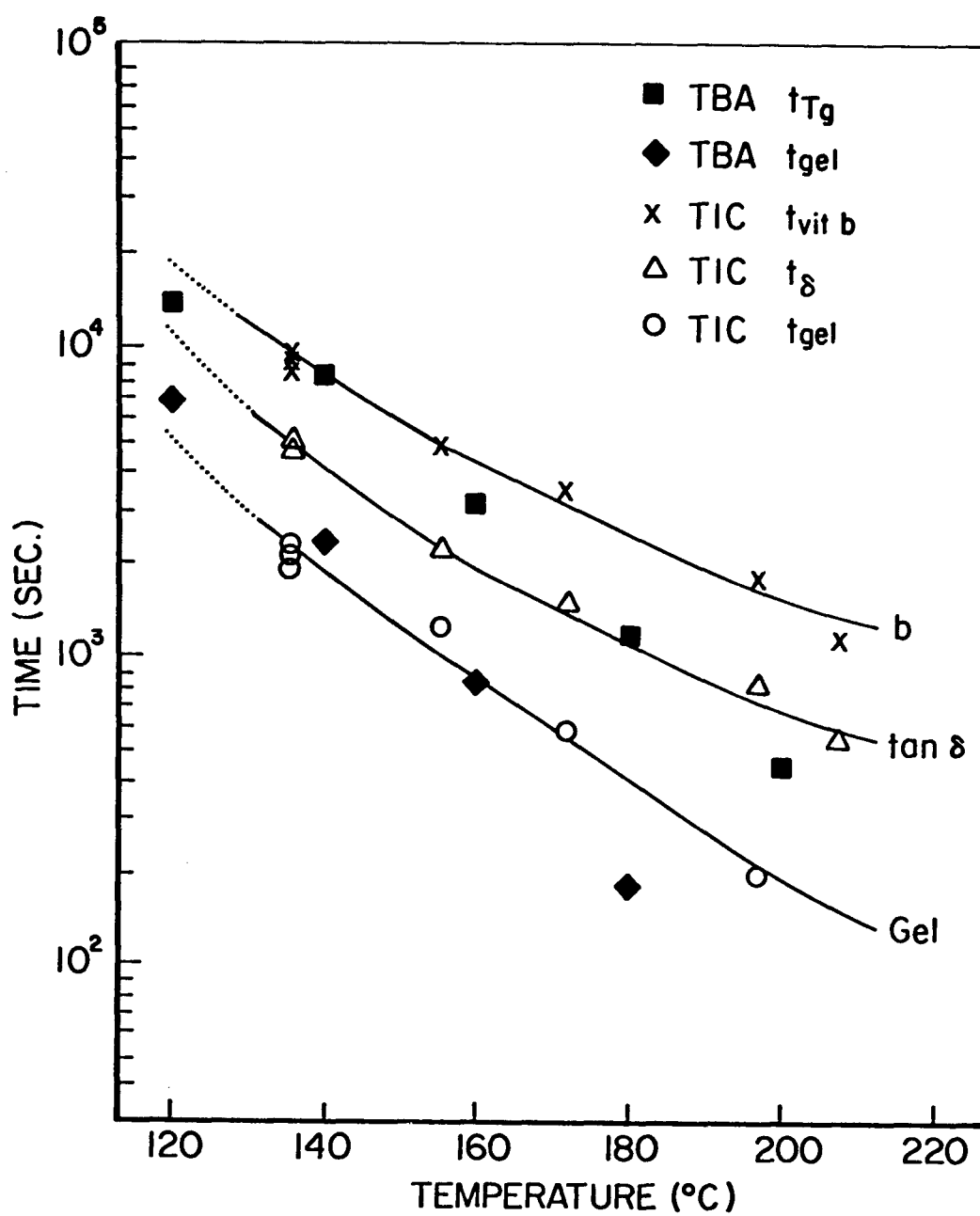| Cure Temperature	t gel	t δ	t vit
135°	2300 sec.	5300 sec.	9000 sec.
155°	1400 sec.	2500 sec.	4850 sec.
175°	600 sec.	1600 sec.	3700 sec.
195°	200 sec.	900 sec.	1900 sec.
207°	---	560 sec.	1200 sec.

Figure 7: The Cure Phase Diagram of Epoxy Constructed with the TICA Results. Results from TBA data on the same system are displayed for comparison.

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are not negligible in comparison with the total reaction time. At low temperatures, the t_{gel}'s agree reasonably well, but the TICA t_δ's and TBA t_{Tg}'s do not. The TBA t_{Tg}'s agree better with the TICA t_{vit}'s. More definitive comparison between the two techniques is not made at this time because of lack of appropriate data.

CONCLUSION

The results of a forced torsion experiment to study polymeric behavior supported on a glass cloth were presented. This technique, called Torsion Impregnated Cloth Analysis, has been demonstrated with thermoplastics as well as thermosetting polymers. The sample preparation procedure, which is an improved version of an earlier reported procedure, is outlined in Appendix I. A partial comparision was made with the TBA results. The results are somewhat different from those of TBA, but it provides just as much versatility as the TBA. Because of the multi-frequency scans and constant frequency capabilities, TICA is very useful in highlighting kinetics effect on the mechanical properties during an experiment.

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APPENDIX I

TICA SAMPLE PREPARATION

1. The cloth used was manufactured by J. P. Stevens and Co., Inc., Style 120-38 (Crowfootweave - unfinished), Piece #1266-01-02.

2. The cloth was cut from a roll of the fabric as a strip of about 6 inches wide and with the same length as the woof (fill).

3. All broken woof are removed from both ends. Additional woof is removed until the area of the fabric covered with woof is about 3½ inches in length.

4. Trim back the warp to about ¼ inch extending on both ends.

5. Remove 10 strands of warp at about 1½ inches from one side of the cloth. Measure a distance of 2.8 inches from the last strand removed and pull another 10 strands of warp (so there will be 2.8 inches of warp in-between).

6. Continue the 10 strands - removal procedure across the cloth. When finished, there should be twelve patches of 2.8 in x 3.5 in area separated by regions without warp.

7. Remove 5 strands in the middle of each patch, (see Picture 2).

8. Clamp both ends of the cloth between glass plates and soak the cloth in the solution of the resins to be studied.

9. Hang the cloth (making sure the warp and woof are not distorted) in the hood overnight.

10. Put the cloth under vacuum (using heat if desired) with continuous pumping for a week.

11. Separate the patches by cuting along the regions without warp (the 10 strands regions only) and trim back all extending woof.

12. Fold the patches into strips according to Picture 3, and tape both ends of the strips with adhesive tape to hold the folding in place (Picture 4).

13. Punch two holes on each strip to accomodate the screws holding the steel-plate fixtures.

14. Put three strips between the fixtures and tighten with screws (Aluminum foil can be used between the strips and the fixtures to avoid bonding). A jig is recommended with this step to help align the strips.

15. Use a vise to tighten the fixtures until the dimensions at both ends of the specimen is suitable for mounting on the RMS.

16. Cut off the portions extending from both ends of the fixture (Picture 5). The TICA specimen is ready to be mounted on the RMS.
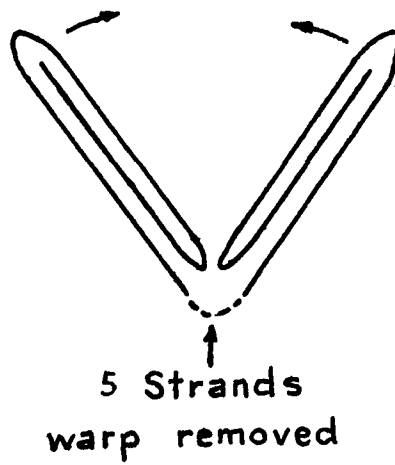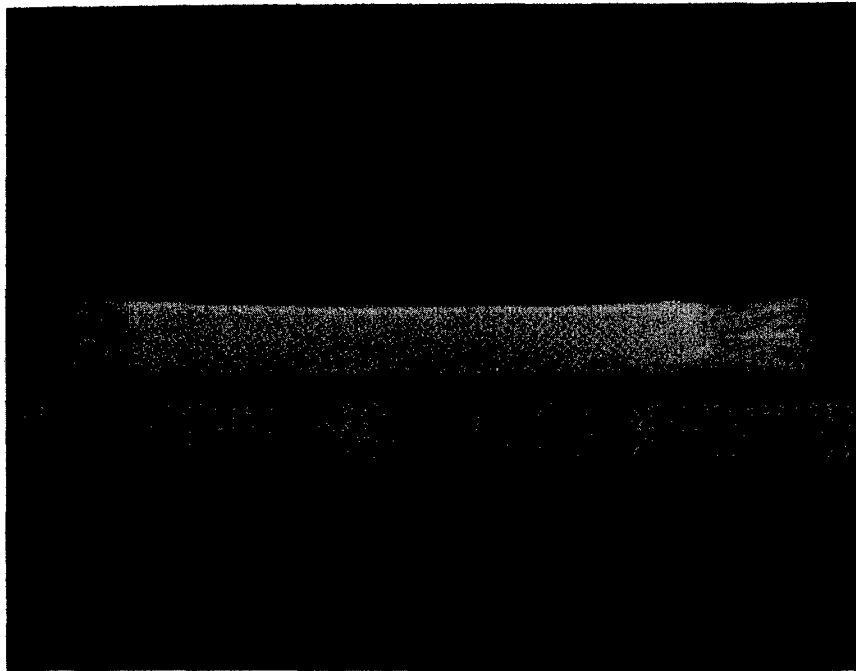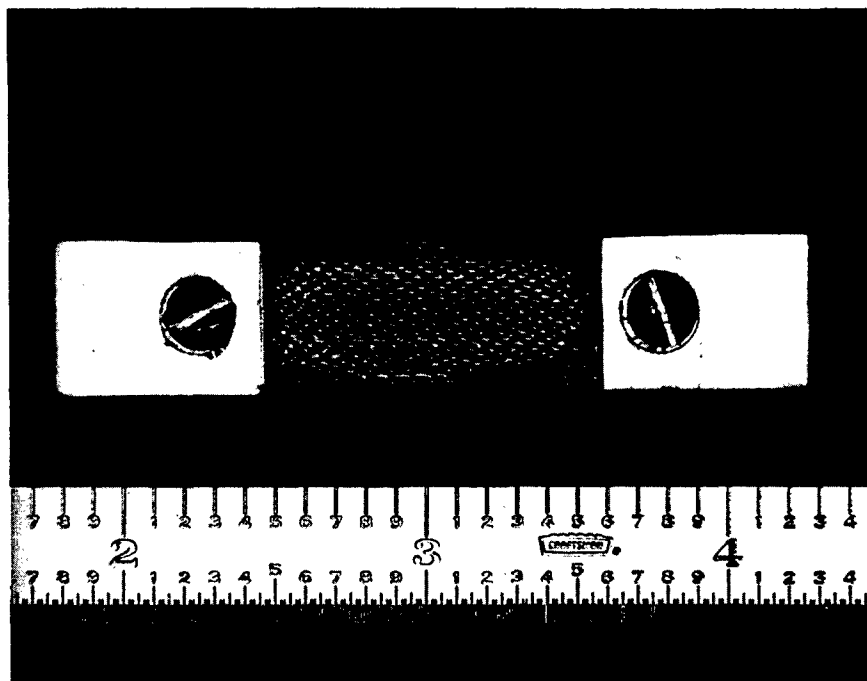
roll of fabric

cut

woof
(fill)

warp (6 inches)

Picture 1

PICTURE 2

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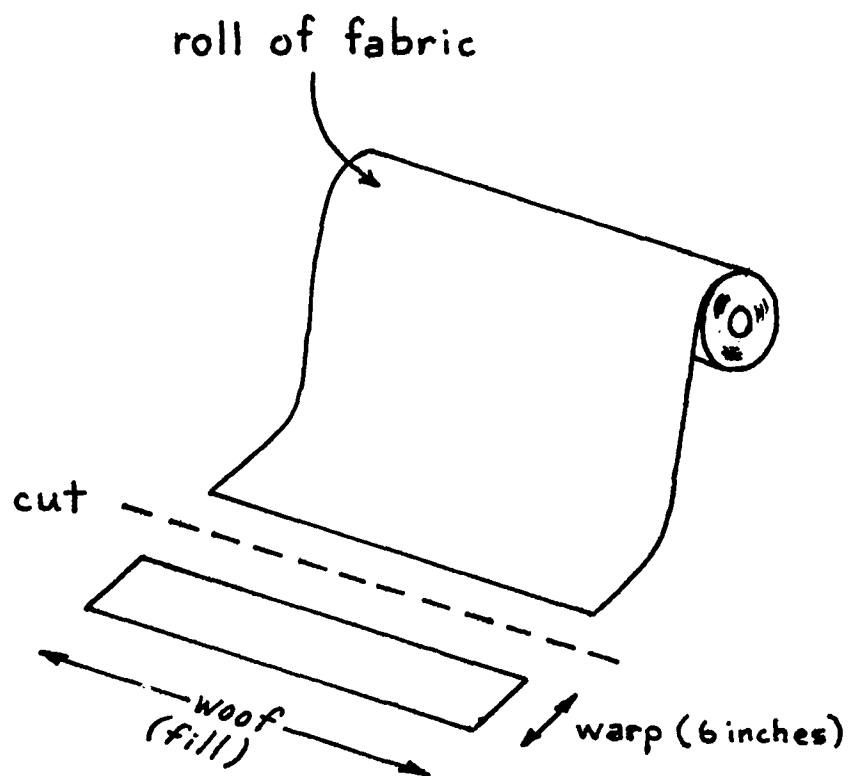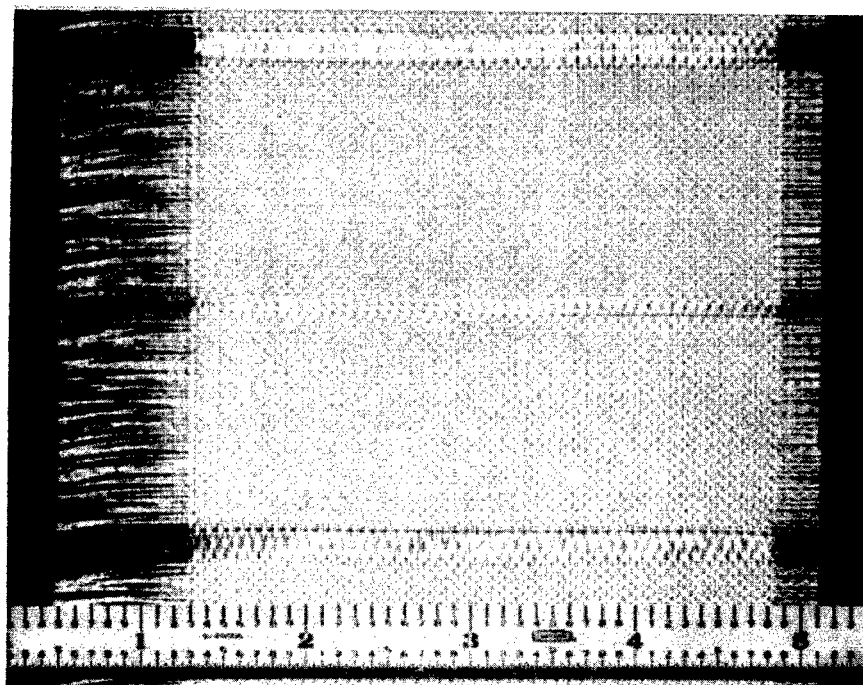
Edge View of Folding

5 Strands
warp removed

Picture 3

PICTURE 4

PICTURE 5